

SHAPE-SELECTIVE ISOPROPYLATION OF NAPHTHALENE OVER DEALUMINATED MORDENITES

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INTRODUCTION

In effort to enhance the economic feasibility of coal liquefaction we are continuing the investigation of non-fuel applications for coal-derived liquids (CDL). Conversion of a small fraction of the naphthalene can significantly increase value, while the majority of the CDL is used as transportation fuel. This study is aimed at the regioselective alkylation of naphthalene. Of particular interest is 2,6-diisopropylnaphthalene (2,6-DIPN) that, when oxidized to the corresponding diacid, can be polymerized to produce high-value engineering plastics and liquid crystalline polymers.¹ Mordenites having high selectivity for 2,6-DIPN production have been reported in a patent by Fellmann et al. at Catalytica, Inc.² However, fundamentals of the alkylation process are poorly understood.

Our research is directed at optimizing 2,6-DIPN selectivity through control of reaction parameters. Effects of temperature, identity of the alkylating agent, naphthalene to catalyst ratio, and addition of water are discussed. An understanding of catalyst physical and chemical properties is pertinent to the design of shape-selective catalysts. Beyond chemical analysis, X-ray powder diffraction has been used to measure crystallinity, cell constants, and crystallite size.

EXPERIMENTAL

Materials. All chemicals were used as supplied. Naphthalene (99 %) and isopropyl alcohol (99.5+ %) were obtained from Aldrich Chemical, Inc. 2,6-Diisopropylnaphthalene (GR) was obtained from TCI, Ltd. Propylene (99.5 % minimum, *polymer purity*) was obtained from Matheson, Inc. and delivered to the reactor in vapor form.

Catalysts. Sodium and hydrogen mordenites were supplied as 9-10 μm average particle size powders (The PQ Corporation, Inc.). Properties of these materials are listed in Table 1. The H-form of NaM14 was obtained by sodium-exchange with 1 M NH_4Cl , followed by wash, dry and calcine procedures. Dealumination of HM14 was accomplished by stirring in aqueous hydrochloric or nitric acid at reflux temperature. Time and acid concentration were varied to control the extent of aluminum removal as summarized in Table 2. Following the acid treatment, the catalysts were washed extensively with hot deionized water, dried, and calcined (5.5 h at 465 °C unless otherwise specified). Samples were dissolved using lithium metaborate fusion and analyzed for silicon, aluminum and sodium by ICP-AES.

Catalyst Evaluation. A 30 cm^3 , stainless-steel tubing bomb, batch reactor was used for all experiments. The standard reactor charge was 0.10 g catalyst, 1.0 g (7.8 mmol) naphthalene, and 0.66 g (15.6 mmol) propylene. For runs with added deionized water, the catalyst amount was increased to 0.15 g. The reactor was mounted on a holder and immersed in a fluidized sand-bath heater. During the run, the reactor was agitated at 3.3 cps. Test conditions were typically a 2 h run at 200 °C. At the end of the test, the reaction was quenched in cold water. The reaction products were collected in acetone solution and analyzed by GC-MS and GC-FID for qualitative and quantitative analyses, respectively. The GC column was 30 m x 0.25 mm DB-17 (J&W Scientific).

RESULTS AND DISCUSSION

Catalysis Test Results. Activity, selectivity and regioselectivity are compared in Table 3 for all of the catalysts in 2 h runs at 200 °C. HM110 and HM230 were run both 2 and 4 h, at 200, 250 and 275 °C. The first five lines of Table 3 detail the results for dealumination of HM14, while the other tests refer to HM38, and HM54 and its dealumination. Isopropyl-substituted naphthalenes (IPN's) constituted 95-99+ % of the products. The major side products were alkyl-substituted naphthalenes (RNAP's) other than *solely* isopropyl-substituted naphthalenes. Disproportionation of IPN's and reaction between naphthalene and propylene dimer (or oligomer) are likely the main sources for RNAP's. Mass balances of less 100 % were primarily due to material loss as carbonaceous deposits on the catalysts, and to a lesser extent, uncharacterized minor products.

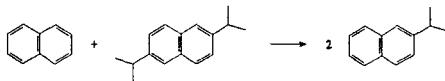
Comparing the 2 h/200 °C data, naphthalene conversion increases slightly or remains unchanged with mild dealumination, but decreases markedly at higher levels of dealumination. HM230 shows higher activity than what is predicted by the trend observed for HM70-HM110, but this may be due to structural changes as discussed below. Similar volcano plots of activity vs. $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio have been reported for reactions of aromatics over mordenites.^{3,4} One explanation for this behavior involves the number and nature of acid sites. Acid site density decreases, and acid

strength increases, with aluminum removal leading to an increase in activity. Ultimately, activity is suppressed by gross depletion of acid sites at high levels of dealumination. Other justifications focus on factors that effect diffusion: changes in mesopore volume, changes in channel structure and dimensions (or channel collapse at high levels of dealumination), and differing rates of fouling. Regardless, the height and position of the activity maximum is dependent upon the reactant, reaction conditions and catalyst preparation.³

Dealumination increases the regioselectivity for β -alkylation (% β -alkylation): % 2-isomer in the monoisopropyl (MIPN) product and % 2,6-isomer in the diisopropyl (DIPN) product both increase. Third (TRIPN) and fourth (TEIPN) isopropylations are also generally diminished, substantially in some cases. Changes in the polyalkylated product with dealumination are nicely illustrated in Figure 1(a)-(c). The larger unlabeled peaks on either side of 2,7- and 2,6-DIPN are isomeric DIPN's. There are ten possible isomers. Fellmann et al. have observed similar changes in DIPN and TRIPN+ distributions with dealumination.² The main DIPN products are the 2,6- and 2,7-isomers. Non-selective catalysts produce nearly equal amounts of these isomers.^{2,5} As observed here and elsewhere,^{2,6,7} the 2,6/2,7 ratio greatly exceeds unity for shape-selective catalysts. It has been suggested by Song et al. that 2,6-DIPN is slightly smaller and may diffuse more rapidly than 2,7-DIPN.⁷ Interestingly, the 2,6/2,7 ratio reaches a maximum at $\text{SiO}_2/\text{Al}_2\text{O}_3$ ca. 71 for 200 °C runs, even though % β -alkylation continues to increase at higher dealumination levels.

Alkylation regioselectivity depends on the nature of the catalyst, catalyst charge, temperature, time and water content. Typically, % 2- in MIPN does not exceed 90% unless the catalyst and reaction conditions are optimized.^{2,5,8} For naphthalene substitution by isopropyl bromide over mordenite at 200 °C, Moreau et al. report nearly 100 % selectivity for the 2-isomer in the MIPN product.⁵ They used a naphthalene/catalyst (N/C) mass ratio of 0.64. We tested HM38 with N/C = 0.62 at 200 °C, and compared the results with our standard run conditions (N/C = 10) at comparable conversion. As shown in Table 4, decreasing N/C dramatically increases % β -alkylation. However, there is a concurrent 11 % decrease in the 2,6/2,7 ratio.

At 25 °C, the equilibrium MIPN isomer distribution is 98.5 % 2-isomer.⁹ Substitution at the more active α -positions of naphthalene leads to the kinetic product. Fellmann et al. obtained the following equilibrium product distribution over amorphous $\text{SiO}_2\text{-Al}_2\text{O}_3$ at 275 °C: 37 % 2,6- in DIPN with 2,6/2,7 of 1.0. Our results for N/C = 0.62 follow the trends discussed by Fellmann et al. with N/C = 90. Conversion increases, while both the % 2,6- in DIPN and the 2,6/2,7 ratio decrease over time. These changes are apparently equilibrium driven. Whereas Fellmann et al. do not comment on changes in the MIPN isomer ratio, we observe an increase in the relative amount of the 2-isomer with time. This may be due to either a higher rate for 1-MIPN \rightarrow 2-MIPN isomerization than for alkylation of 2-MIPN, or transalkylation between 2,6-DIPN and naphthalene.



With N/C = 10, there simply are not enough appropriate acid sites available for rapid isomerization of the kinetic 1-MIPN product. The %2- in MIPN is low, and consecutive alkylation does not give a DIPN product distribution enriched in the 2,6-isomer. From Table 3 (N/C = 10), conversion increases with time over HM110 and HM230, while % β -alkylation and the 2,6/2,7 ratio remain approximately constant with time. Although not shown here, the same trends were observed for HM38 with N/C = 10.

Increasing the reaction temperature to 250 or 275 °C (Table 3) causes a substantial increase in conversion. The 2,6/2,7 ratio increases markedly, and % β -alkylation is mildly increased. It may be concluded that 2,6-DIPN is thermodynamically more stable, and 2,7-DIPN is the kinetic product.

In separate experiments, we examined the fate of 2,6-DIPN over three mordenites in 2 h, 200 °C reactions. Table 5 shows that the principle reaction is alkylation. At low propylene pressure, isomerization does occur over HM14 and HM38, principally to DIPN isomers other than 2,7-DIPN. Higher propylene pressures retard isomerization—an effect also demonstrated in propylene addition to biphenyl.¹⁰ Dealuminated mordenite, HM74, gives almost no isomerization. The % 2,6-DIPN remains high, while other DIPN isomers react to form higher alkylates. Over aluminum-deficient mordenites, 2,6-DIPN is apparently less reactive toward alkylation than other DIPN isomers. This is not the case for HM14 and HM38 where 10-30 % of 2,6-DIPN is converted, mostly to higher alkylates. Structural analysis of the TRIPN isomeric products, from isotopically labeled DIPN if necessary, would aid the interpretation of these results.

In related work on the isopropylation of naphthalene over HM38 and other zeolites, we have observed higher β -alkylation selectivities and higher 2,6/2,7 ratios for isopropyl alcohol, rather than propylene addition.⁷ Byproduct water is inherent when alcohols are used. To test the hypothesis that the presence of water enhances regioselectivity, a series of experiments were performed where the amount of catalyst, naphthalene, and propylene in the reactor were held constant. Water was added

in various amounts. Catalyst mass in the reactor was increased to 0.15 g for these experiments to amplify the changes brought about by water addition. Changes in the polyalkylated product distribution with added water are illustrated in Figure 1(d)-(f) and Table 6. A small amount of water poisons the catalyst, but larger amounts bolster activity up to an apparent saturation limit. The maximum in activity is approximately at 160 mg added water—very close to the mass of catalyst in the reactor. A possible explanation is that at low partial pressures, water adsorbs on catalytic acid-sites and impairs adsorption of reactants. Higher partial pressures of water lead to the genesis of new Brønsted acid catalytic sites, leading to higher conversion. Ultimately, high moisture levels reduce conversion due to impeded reactant diffusion. This proposition may also explain the increase in β -alkylation selectivity and 2,6/2,7 ratio with added water. Adsorption of water impedes reaction on the non-selective external surface of the catalyst. A higher percentage of the naphthalene molecules react within the shape-selective confines of the mordenite channels. Adsorption of water within the mordenite channels impedes diffusion. More so in the case of the larger α -, α,β -, and α,α -substituted products. The result again is higher % β -alkylation. It is unclear why the 2,6/2,7 ratio drops sharply above 160 mg added water, even though % β -alkylation does not. However, throughout this work there is a positive correlation between the 2,6/2,7 ratio and conversion. Our preliminary data show that the regioselectivity enhancement resulting from added water is even more pronounced for less shape-selective mordenites.

Catalyst Characterization by XRD. Four of the catalysts have been examined by XRD (Cu K α radiation): HM14, HM74, HM110 and HM230. Overall, XRD shows that dealumination following calcination at 700 °C causes a partial structure collapse that is not observed for samples calcined at 465 °C. Estimates of mean crystallite dimension were made using the Scherrer equation, assuming Cauchy profiles. Average results for measurements on the six strongest, well-resolved reflections are reported here. Natural sodalite was used as a standard for instrumental line broadening. Within error of measurement, HM14, HM74 and HM110 are of the same crystallite size, 230 \pm 20 nm. However, HM230 crystallites are smaller, 140 \pm 10 nm.

Comparison of the area sum for the six peaks allows an estimate of relative crystallinity. HM230 is approximately only two-thirds crystalline material; whereas, the other three samples are of the same relative crystallinity (assumed 100%).

Least-squares regression analyses were used to obtain precision measurements of the cell constants from the diffraction data. It is only possible to compare relative differences between the samples at this time (see Figure 2), since the data have not been zero- nor background-corrected. As summarized by Mishin et al., dealumination of mordenites results in a lattice contraction that is generally anisotropic.³ Our data show that changes in the a-dimension are the largest. Decreases in b and c are similar, but smaller than for a. HM230 showed the largest magnitude lattice contraction. HM74 and HM110 show the same overall cell volume decrease. The contraction is isotropic for HM74; whereas, for HM110 and HM230, it is not.

CONCLUSIONS

We have succeeded in identifying several important parameters that govern selectivity in the addition of propylene to naphthalene. The naphthalene/catalyst ratio (N/C) has significant impact on the resulting β -alkylation selectivity. For a given N/C, the 2,6/2,7 ratio closely parallels naphthalene conversion. Yield of 2,6-DIPN was inherently higher for N/C = 0.62, but both % 2,6- in DIPN, and the 2,6/2,7 DIPN isomer ratio decrease over time. Increasing N/C to 10 requires shape-selective dealuminated mordenites and reaction temperatures in excess of 200 °C to obtain good 2,6-DIPN yields. Longer reaction times increase conversion and DIPN yield, while MIPN and DIPN isomer distributions do not change. The 2,6/2,7 ratio increases with temperature, indicating that 2,6-DIPN is thermodynamically more stable. With N/C = 10, 2,6-DIPN is neither isomerized nor alkylated to any appreciable extent over high-silica mordenites. We have also found that addition of water to the reactor, in amounts up to approximately the mass of catalyst, results in substantial gains in regioselectivity.

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Table 1. Properties of the Mordenite Starting Materials¹

catalyst	SiO ₂ /Al ₂ O ₃ , molar	Na ₂ O, wt %	surface area, m ² /g	porosity, cm ³ /g	
				meso ²	micro ³
NaM14	14.3	6.24	466	0.14	0.17
HM38	37.5	0.07	512	0.13	0.17

¹Data as reported by the supplier. ²Meso refers to 20-600 Å pores. ³Micro refers to < 20 Å pores.

Table 2. Preparation and Composition of Mordenite Catalysts Used in This Work

catalyst	treatment ¹	SiO ₂ /Al ₂ O ₃ , Na ₂ O, molar wt %	
HM14	exchange NaM14 with 1 M NH ₄ Cl	13	0.19
HM54	stir NaM14 in 1 M HCl for 24 h at reflux	54	0.15
HM70	stir HM14 in 1 M HCl for 5 h at reflux	70	< 0.01
HM71	stir HM14 in 1 M HCl for 10 h at reflux	71	< 0.01
HM74	stir HM14 in 1 M HCl for 24 h at reflux	74	< 0.01
HM90	stir HM14 in 3 M HCl for 24 h at reflux	90	< 0.01
HM110	calcine HM54 at 465 °C, then stir product in 6 M HNO ₃ for 24 h at reflux. Final calcination at 465 °C.	110	< 0.01
HM230	calcine HM54 at 700 °C, then stir product in 6 M HNO ₃ for 24 h at reflux. Final calcination at 700 °C.	230	< 0.01

¹All catalysts calcined 5.5 h at 465 °C unless otherwise specified.

Table 3. Results for Propylene Addition to Naphthalene¹

Table 3. Results for Propylene Addition to Napthalene											
catalyst	T, °C	time, h	%NAP conv	product distribution, molar basis							2,6/2,7 ratio
				% yield		% MIPN	% DIPN	% TRIPN+	% 2- in MIPN	% 2,6- in DIPN	
				IPN's	RNAP's						
HM14	200	2	76	67	0.9	64	33	3.6	60	33	1.76
HM70	200	2	83	69	1.4	53	41	5.7	59	44	2.17
HM71	200	2	74	65	1.2	61	37	2.3	64	51	2.29
HM74	200	2	47	41	0.5	76	23	0.6	71	55	2.24
HM90	200	2	36	32	0.3	80	19	0.9	70	53	2.21
HM38	200	2	73	61	1.0	61	34	4.5	58	39	1.99
HM54	200	2	43	41	0.6	76	23	1.2	68	50	2.11
HM110	200	2	15	16	0.2	85	15	0.4	83	61	2.05
HM110	250	2	28	28	0.6	79	21	0.6	86	65	2.48
HM110	275	2	46	42	1.5	71	28	1.0	87	66	2.67
HM110	200	4	19	19	0.3	83	17	0.4	83	61	2.09
HM110	250	4	39	36	1.1	75	25	0.7	86	65	2.48
HM110	275	4	58	51	2.3	66	33	1.3	87	65	2.64
HM230	200	2	41	40	0.8	74	25	1.1	74	58	2.32
HM230	250	2	63	58	1.2	59	39	2.3	78	62	2.57
HM230	275	2	76	67	1.6	49	47	4.0	79	62	2.58
HM230	200	4	49	46	0.9	70	29	1.2	73	59	2.37
HM230	250	4	75	68	1.7	50	46	4.3	75	60	2.51
HM230	275	4	84	74	1.9	41	54	4.4	78	62	2.54

¹Catalyst charge 0.10 g.

Table 4. Comparison of HM38 Using Different Naphthalene to Catalyst Ratios at 200 °C									
reactor charge	%NAP conv	product distribution, molar basis							
		% yield		%	%	%	% 2-	% 2,6-	2,6/2,7
		IPN's	RNAP's	MIPN	DIPN	TRIPN+	in MIPN	in DIPN	ratio
1.00 g naphthalene and 0.10 g HM38	90	75	1.1	46	46	7.2	53	38	2.06
0.62 g naphthalene and 1.00 g HM38	88	67	2.5	51	46	3.4	90	52	1.85

Table 5. Reaction of 2,6-Diisopropylnaphthalene Over Mordenites in 2 h, 200 °C Runs ¹								
catalyst	propylene/ 2,6-DIPN, molar	product distribution, molar basis						
		% MIPN	% 2,6-DIPN	% 2,7-DIPN	% other DIPN	% TRIPN	% TEIPN	% RNAP
none start. mat'l.	—	3.48	95.46	0.39	0.31	0.17	0.00	0.19
HM14	4.0	0.00	69.58	0.09	0.26	26.06	3.67	0.33
HM14	1.0	0.11	71.18	0.29	1.93	23.40	2.77	0.32
HM14	0.5	0.43	72.61	1.06	4.57	19.09	1.93	0.31
HM38	4.0	0.19	71.59	0.11	0.29	24.92	2.73	0.17
HM38	1.0	2.22	73.65	0.20	1.15	19.61	1.93	1.25
HM38	0.5	0.12	83.54	0.21	1.25	13.44	1.18	0.25
HM74	4.0	0.00	94.72	0.07	0.09	4.42	0.46	0.24
HM74	1.0	0.01	96.67	0.08	0.13	2.58	0.26	0.26
HM74	0.5	0.00	96.87	0.09	0.22	2.35	0.23	0.25

¹ Reactor charge: 1.00 g (4.71 mmol) 2,6-diisopropylnaphthalene, 0.10 g catalyst, and varied propylene pressure.

Table 6. Propylene Addition to Naphthalene Over HM74 in 2 h, 200 °C Runs with Various Amounts of Added Water ¹									
added water, mg	%NAP conv	product distribution (molar basis)							
		% yield		%	%	%	% 2-	% 2,6-	2,6/2,7
		IPN's	RNAP's	MIPN	DIPN	TRIPN+	in MIPN	in DIPN	ratio
0	56	51	1.2	69	29	1.7	67	53	2.24
10	40	38	0.7	77	23	0.7	75	59	2.22
40	33	32	0.6	79	21	0.6	80	64	2.37
50	29	28	0.6	77	23	0.8	80	63	2.38
100	45	42	0.9	75	25	0.5	84	68	2.61
120	54	52	1.2	73	27	0.5	84	69	2.62
120	55	51	1.2	72	28	0.5	84	69	2.65
160	59	54	1.4	72	28	0.4	84	68	2.56
300	22	22	0.3	88	12	0.1	86	66	2.15

¹ Catalyst charge 0.15 g.

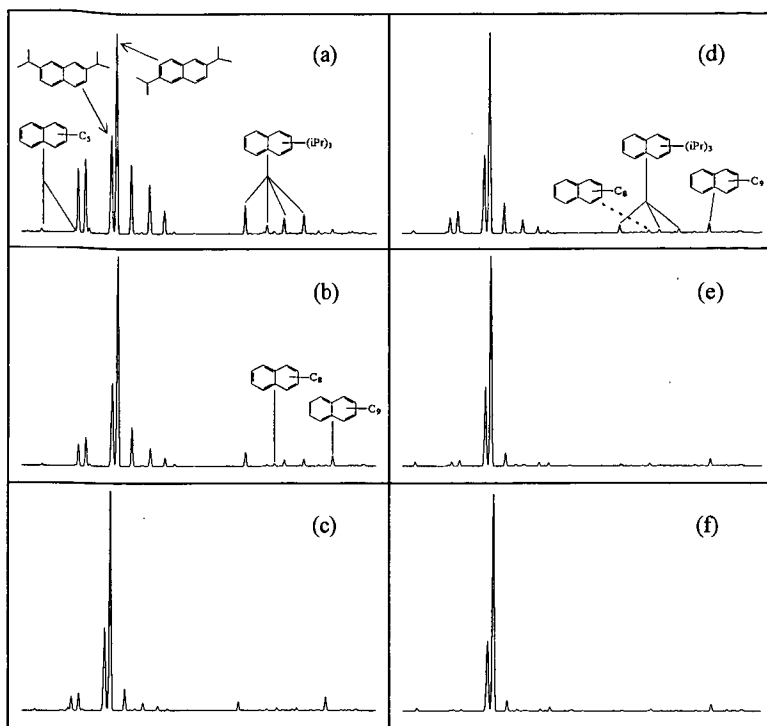


Figure 1. Comparison of the polyalkylated naphthalene region of the gas chromatograms for 2 h catalytic runs at 200 °C, 1 g naphthalene, and propylene/naphthalene = 0.5. Parts (a) through (c) are neat runs with 0.10 g catalyst charge: (a) HM14, (b) HM71, and (c) HM230. Parts (d) through (f) compare 0.15 g HM74 charge with (d) no added water, (e) 40 mg added water, and (f) 120 mg added water.

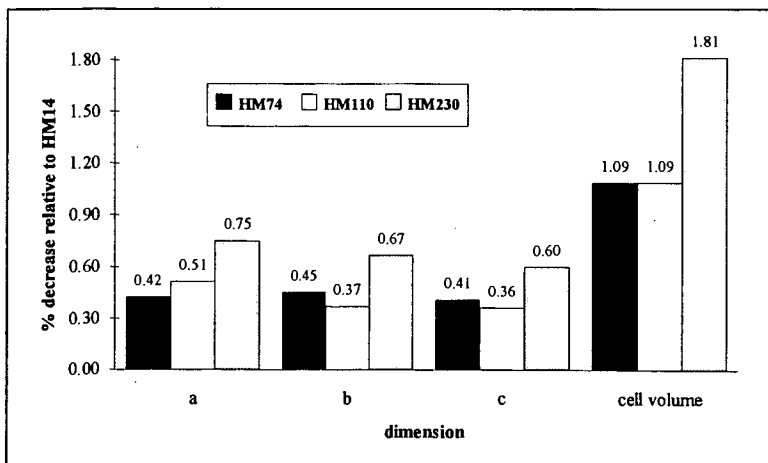


Figure 2. Percentage decreases in cell constants and cell volumes as a result of dealumination. Calculations relative to the cell dimensions determined for HM74.